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micrograms/cu.m micrograms/cu.m micrograms NO2/cu.m

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Collaborative Testing of a Manual Sodium Arsenite Method for Measurement of Nitrogen Dioxide in Ambient Air

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■ The sodium arsenite method for 24-h integrated measurement of NO_2 in ambient air was subjected to a collaborative test. Ten collaborators sampled ambient air and simultaneously the same ambient air spiked with a reliable source of NO_2 for 4 days at a common site in Kansas City, Mo. NO_2 concentrations of 50–370 $\mu g/m^3$ were sampled. Within and between laboratory standard deviations were 8 and 11 $\mu g/m^3$, respectively, over the range 84–312 μg NO_2/m^3. The method had a bias of −3% of the concentration over the above range. The lower detectable limit (LDL) of the method was 8 $\mu g/m^3$. The test results indicated that the method will produce accurate, precise measurements of ambient NO_2 concentrations.

On July 14, 1972, the U.S. Environmental Protection Agency (EPA) withdrew the EPA promulgated (*1*) reference method for measuring atmospheric concentrations of nitrogen dioxide (NO_2) because of demonstrated inadequacies in the procedure (*2, 3*). After withdrawal, EPA embarked on an extensive program to develop a replacement for the original reference NO_2 method and selected five candidate procedures: a manual arsenite procedure, a manual triethanolamine-quiacol-sulfite procedure, a manual triethanolamine procedure, a continuous chemiluminescence procedure, and a continuous colorimetric procedure.

This paper reports work on evaluation of the manual arsenite procedure. The first phase of the work, a laboratory investigation to develop specifications and procedures for the use of the method and the incorporation of the results in a detailed method write-up describing the proper use of the method, has been reported (*4*). The second phase of the work involved subjecting the method to a collaborative test to determine its bias and precision in the hands of a group of typical users and is the subject of this paper.

Experimental Procedure

Sampling System for Collaborative Test. A diagram of the sampling system is shown in Figure 1. Incoming ambient air is split into a spiked and unspiked line with a sampling manifold near the end of each line. The spike was generated by adding known amounts of NO_2 at a constant rate over a 24-h period from permeation devices maintained at 25.1 ± 0.1 °C. These devices were obtained from the National Bureau of Standards (prototype of Standard Reference Material 1629). Since the spike concentration of NO_2 was used as the standard against which bias was determined, its integrity had to be established. Teflon parts were used downstream from the injection of the spike to minimize loss of NO_2 to the walls, and a high constant flow rate of 60 L/min of ambient air was maintained through the spiked line. The high flow rate and consequent short NO_2 residence time minimize loss of NO_2 by reaction with water vapor and allow an ample excess of sample over that being taken by the collaborators.

The integrity of the spike was checked before and during the test by monitoring the NO_2 concentration in the spiked and unspiked manifold with a Bendix NO_2-chemiluminescent monitor, as shown in Figure 1. The difference in NO_2 concentration between the spiked and unspiked manifolds was within 5 $\mu g/m^3$ (limit of instrument sensitivity) of that predicted by the gravimetric permeation rate and the air volume; therefore, the latter data were used to determine the spike values. Additional details on design of the sampling system can be found in the referenced report (*5*).

Discussion

Collaborative Test. Collaborative testing has long been recognized as an effective way of determining the statistical limits of error inherent in an analytical method (*6*). To provide useful information on the performance of a method, an adequate number of test participants, that are representative of the average user community using the method, should be selected. Ten volunteer collaborators were selected to participate in the test. The selection was based primarily on past experience in use of the method, ability to furnish equipment necessary to perform the test in accordance with the method, and type of organization. Seven of the collaborators selected were from state and local organizations, two from industrial laboratories, and one from a government laboratory. The collaborators and their affiliations are given in ref. *5* and are referred to subsequently as collaborators A–J to maintain anonymity.

The test involved sampling ambient air and the simultaneous sampling of the same air spiked with NO_2 for 4 days at a common site in rural Kansas City, Mo. The sampling system is shown in Figure 1. Spikes, nominally 50, 100, 200, and 300 μg NO_2/m^3, were added (one level per day) over a 24-h period to obtain typical ambient NO_2 concentrations. The ambient NO_2 concentration varied from 10 to 50 $\mu g/m^3$ over a 24-h

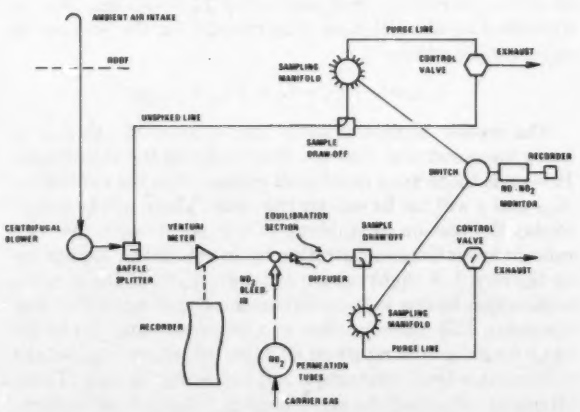

Figure 1. NO_2 sampling system

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Table I. Collaborators' Data; Spike Value 90.9 μg/m³

Sample	Collaborator									
	A	B	C	D	E	F	G	H	I	J
Spiked line	92.4	99.0	112.77	104.08	107.72	103.93	114	121.0	92.9	115.2
	94.2	100.0	106.02	102.36	109.54	84.37	90	114.0	87.2	115.3
	81.0	101.0	102.37	125.62	112.12	103.54	116	113.0	92.9	113.4
	77.4	100.0	107.89	106.37	118.44	103.54	115	118.0	94.2	115.7
Unspiked line	19.3	20.0	21.14	30.49	25.49	23.30	26	28.8	16.6	24.6
	21.4	14.0	22.06	25.31	25.01	23.30	13	28.0	15.0	23.7
Samples supplied to collaborators										
Control = 1.00 μg NO_2/mL	1.092	1.007	1.03	0.51	1.00	1.03	1.01	1.033	1.01	0.994
Blank = 0.0 μg NO_2/mL	0.017	0.0	0.006	0.01	0.0	0.02	0.01	0.012	0.01	0.005

period. Although these values were somewhat low, compared to typical ambient NO_2 levels, the concentration did exhibit the normal variability typical of ambient conditions. Thus, the collaborators were sampling an atmosphere that contained a known recoverable amount of NO_2, and the concentration was changing with time.

The collaborators were provided with a copy of the method and instructed to follow it in detail. Each collaborator prepared absorbing solution at his home laboratory and brought an adequate supply to the test site along with the equipment called for in the method. Collected samples, 24 per collaborator, plus one blank and one control sample (the latter samples were supplied to the collaborators) were returned to the collaborators' home laboratory for analysis. These procedures were used to minimize any biasing of the test results that may have resulted from the collaborators having to work together to collect samples.

Experimental Design. It was desired to determine estimates of both precision and bias. Precision was determined by having all 10 collaborators collect samples from the spiked line at each NO_2 level. Bias was determined at each level by having all collaborators simultaneously collect samples from the ambient and spiked lines (each collaborator had two sampling trains); both samplings were carried out over exactly the same 24-h time period. All data were reported as 24-h average concentrations.

One way to obtain estimates of precision and bias is to express the observed NO_2 concentration as a linear combination of certain variables. Each individual 24-h average, X_{ikj}, is described by the following linear model for the purpose of determining precision:

$$X_{ijk} = \mu + C_i + L_j + CL_{ij} + e_{k(ij)}$$

The model assumes initially that a constant value, μ, is being measured that does not change during the experiment. However, there are a number of reasons that the two values X_{ijk} and μ will not be exactly the same. There will be a day-to-day fluctuation in ambient NO_2 concentration that can raise or lower the concentration by an amount L_j depending on the day, j. A slight raising or lowering, C_i, of the concentration may be due to the collaborator, i, that made the measurement. This difference due to collaborators may not be the same for all collaborators on all days; this effect is called the collaborator-level interaction and is denoted by CL_{ij}. These effects are about all the experimental design allows us to examine. In addition to the above effects, there is usually some unexplained variation that fluctuates randomly each time a measurement is made. This effect is denoted by $e_{k(ij)}$ and is called experimental error. All of these effects are included in the linear model.

Since the collaborators were chosen at random and the days during which the experiments were conducted had no particular significance, we can assume that the model is completely random. The random properties of the model imply that the overall average for each of the effects C_i, L_j, CL_{ij}, and $e_{k(ij)}$ is zero with variances of σ_C^2, σ_L^2, σ_{CL}^2 and σ_e^2, respectively. Statistical theory then tells us that the total variance of an observation is made up of the sum of these components. These components are used to estimate the precision of the method. The components of variance of principal interest were σ_e^2 (variance of repeated observations within a collaborator) and σ_c^2 (variance between collaborator means).

Bias is determined from the collaborators' simultaneous measurements on the spiked and unspiked lines. An individual bias, Z_{ijk}, is determined by first subtracting from a collaborator's response on the spiked line, X_{ijk}, the average of all collaborators' ambient observations over the same time period, $\overline{A}.j$. The spiked level, N_{js}, is then subtracted from this quantity to obtain the deviation from the true value, i.e., a bias. The relationship is expressed as follows:

$$Z_{ijk} = (X_{ijk} - \overline{A}.j) - N_{js}$$

The design for determining bias is subject to error mainly to the extent that $\overline{A}.j$ differs from the "true" ambient level. Additional information on these models can be obtained from ref. 5.

Collaborators' Data. Table I shows one of the four data sets obtained in the test. Each collaborator collected four samples from the spiked line and two samples from the ambient line per 24-h run. The control and blank samples were supplied to the collaborators to provide a separate check on the analytical portion of the method.

Outlying Values. An inspection of all the data submitted revealed that collaborators A and I had much larger negative biases than the other eight collaborators and that these two collaborators made systematic computational errors. An analysis of variance was carried out with data from all 10 collaborators and with collaborators A and I excluded to determine the effect of these computational errors on the components of variance. Including collaborators A and I results had no effect on the standard deviation within a laboratory (collaborator), but significantly affected the standard devia-

Table II. Components of Variance, All NO_2 Levels

Components	Value, $\mu g/m^3$	Relative standard deviation, %	
		84 $\mu g/m^3$	311 $\mu g/m^3$
σ_e	8.2	10	3
σ_c	7.9	...	...
$(\sigma_e^2 + \sigma_c^2)^{1/2}$	11.3	13	4

Table III. Average Bias

True NO_2, concn, $\mu g/m^3$		Bias	
		$\mu g/m^3$	%
	84.1	−5.1	−6
	113.2	−4.7	−4
	228.3	−5.7	−2
	311.7	−9.7	−3
Av	184.3	−6.3	−3

tion between laboratories, σ_c. The values of σ_c were 7.9 $\mu g/m^3$ with 8 and 14.6 $\mu g/m^3$ with 10 collaborators' results, respectively. Data from collaborators A and I were therefore deleted to maintain a data set that represented the capabilities of the method when followed. These computational errors prompted the authors to reexamine the method for clarity of directions on computations. It was concluded that the directions were clear, and no changes in the method description were made. In the remaining data there was one individual outlying value (via the Dixon test (7) at $\alpha = 0.05$) and one missing value. Both of these values were replaced with artificial values (8).

Precision. The assumption of homoscedasticity (equal variance at all NO_2 concentrations) in the analysis of variance model was checked by carrying out an analysis of variance at each of the four NO_2 concentrations and computing the standard deviation within a laboratory, σ_e. With increasing NO_2 concentration these values were 5.4, 7.3, 9.8, and 9.3 $\mu g/m^3$. Thus, the variance is not uniform. It depends on concentration but not in a simple way (5). Since σ_e does not monatonically change with concentration or μ, it is unlikely that any standard data transformation would improve the homoscedasticity. Therefore, no data transformation was applied. Details of the statistical analysis concerning the homoscedasticity of the data have been published (5).

The four data sets were pooled, and the analysis of variance was carried out. *F*-tests were performed to determine the significance of collaborator and collaborator-level interaction variances. The *F*-values for collaborator and collaborator-level were significant; however, the degree of significance may be inflated by nonhomogeneity of the variances. This means that different collaborators had different average NO_2 values and that there was a collaborator-level interaction. However, the interaction is due almost entirely to one collaborator, D (5).

The individual components of variance are shown in Table II. The standard deviation within a laboratory is given by σ_e, and the standard deviation between laboratories is given by $(\sigma_e^2 + \sigma_c^2)^{1/2}$. These values represent the best *average* estimate of the precision that will be obtained with the method over the range 84–311 $\mu g/m^3$. That one value, in $\mu g/m^3$, is given for the complete range should not be interpreted as meaning that the precision is completely independent of concentration. The precision does depend on NO_2 concentration, but not in an easily defined manner, as was discussed earlier.

Using the average value for σ_e and σ_c, the relative standard deviation within a laboratory varies from 10% at 84 $\mu g/m^3$ to 3% at 311 $\mu g/m^3$. Over the same range the relative standard deviation between laboratories varies from 13 to 4%.

Bias. In the model for determining bias, the true value is the NO_2-spiked level plus the average of the collaborators' ambient values. A bias is the difference between a collaborator's reading on the spiked line and the true value. For example, the true value for the spike value of 90.9 $\mu g/m^3$ (Table I) was 113.2 $\mu g/m^3$. The bias for the first reading of collaborator F in Table I would then be 103.9 − 113.2 = −9.3 $\mu g/m^3$.

The bias data are presented in Figure 2, wherein percent bias is plotted against the true values for all eight collaborators. Five collaborators produced negative biases, and three had positive values. Collaborator-level interaction, shown to be significant in the analysis of variance, is indicated by nonparallel lines. Most of this interaction is due to the variable bias exhibited by collaborator D. In other words, although there is a significant collaborator-level interaction, seven of the eight collaborators produced a relatively uniform percent bias irrespective of the NO_2 level. Therefore, the percent bias values for all four levels were averaged. The average value, shown in Table III, was −3%.

Lower Detectable Limit. The lower detectable limit was estimated in two ways. The between collaborator standard deviation from the ambient readings and the standard error of estimate from the collaborators' calibration curves were doubled (5). The two values were 7 and 8 $\mu g/m^3$, respectively. Thus, the smallest NO_2 concentration that can be detected as significantly different from zero when comparing results from different laboratories is approximately 8 $\mu g/m^3$ (0.004 ppm).

Conclusions

The sodium arsenite method exhibits excellent precision, a small negative bias, and an acceptable lower detectable limit for monitoring ambient levels of nitrogen dioxide. The method is a reliable procedure for making 24-h integrated measurements of nitrogen dioxide in ambient air.

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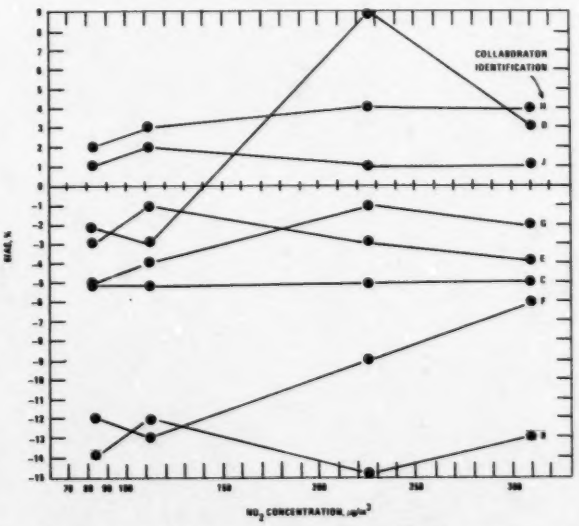

Figure 2. Collaborator bias as a function of NO_2 concentration

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